

DATA EVALUATION REVIEW 3

I. Study Type: photolysis, soil

II. Citation:

Stumpf, K. Hoe 039866 - ^{14}C , Photodegradation on Sterile Soil. performed by Hoechst AG, Frankfurt am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 5/17/89. Received EPA 12/12/89 under MRID # 413231-16.

Stumpf, K. Hoe 039866 - ^{14}C , Photodegradation on Non-Sterile Soil. performed by Hoechst AG, Frankfurt am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 9/6/89. Received EPA 12/12/89 under MRID # 413231-17.

III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

E.B. Conerly 5/10/90

IV. Conclusions: The study is not acceptable to fulfill the requirement for soil photolysis data, for reasons detailed below. A new study is required under conditions more nearly approximating use rates. The current study does provide some information:

- 1) Glufosinate ammonium is subject to light-mediated degradation on the surface of a soil containing an active microbial population, but not on a "sterile" soil.
- 2) Under the experimental conditions, the half-life in a sandy loam soil was 35 - 36 days natural sunlight equivalent (moderately labile).
- 3) The percentage of unextractable radioactivity increased over time to ca 30%.

V. Materials and Methods:

test compound -- ^{14}C labelled in the 3 and 4 positions
sterile soil -- sandy loam "which had been sterilized"
non-sterile soil -- the same, but not sterilized
plate preparation -- soil was passed through a 2 mm sieve, made into a slurry, and coated onto 4 x 4 cm stainless steel plates which were dried overnight. The approximate weight of soil on one plate was 1.5 gm, and bulk density was 1.15 g/cm³ [Therefore the soil layer was 1.5/1.15 cm³ = 1.30 cm³. The thickness of the soil layer was 1.30 cm³ volume / 16 cm² surface area = .08cm = 0.8 mm]. 51 ug of test compound (ca 30 ppm)
light source -- xenon arc lamp with 290 nm cut-off filters
exposure conditions -- 25±5°C, 120 hours (corresponding to 32 days). The experimental set up provided irradiation which was approximately 1.5 x more intense than sunlight

VI. Study Author's Results and/or Conclusions:

The soil photolysis of HOE 039866 was studied to determine the route and velocity of degradation and the nature of photolytic products.

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RESULTS:

Sterile soil -- Formation of $^{14}\text{CO}_2$ amounted to about 2.3% of the applied radioactivity at the end. No further degradation products were observed. Dark controls showed no release of $^{14}\text{CO}_2$.

Non-sterile soil -- the calculated half life was 35 - 36 days under natural sunlight. Of the six degradation products detected, three were identified as the soil metabolites HOE 061517, HOE 064619, and HOE 085355. Three other degradates were each less than 10% of applied. Formation of CO_2 amounted to 7.6% of the applied at the end of irradiation. Corresponding dark controls did not release CO_2 , and HOE 061517 was measured at 0 - 8%.

CONCLUSIONS:

HOE 039866 is subject to photodegradation on soil surfaces with a half life of 35 - 36 days under outdoor conditions. Mineralization to CO_2 and six metabolites shows that photodegradation takes place. The fact that HOE 039866 shows photolytic breakdown on soil surfaces, in contrast to its behavior in sterile buffer solution and on a sterile soil surface, is best explained by photoactivation by compounds (such as humic acid) in the soil, since HOE 039866 has no UV absorption at wavelengths >290 nm.

VII. Reviewer's Comments:

- 1) The study was performed at a concentration many times higher than the expected label rates and also approximately three times the highest rate used in the metabolism studies. The rate of metabolism is known to decrease with increasing concentration of Glufosinate ammonium, and this could be due to adverse effects on the soil microbes.
- 2) The dark, non-sterile, control is in effect a soil metabolism specimen and should reflect that process. Accordingly, it should yield a half-life somewhere in the range observed for soil metabolism studies, 3 - 30 days. Instead, it indicates a half-life somewhere around 300 days, pointing to an almost complete lack of metabolism in these specimens. This could be more evidence of an adverse effect on soil microbiota.
- 3) On the other hand, the observed decomposition cannot be explained solely by chemical photosensitization due to compounds in the soil, since degradation does not occur in the "sterile" light-exposed samples.
- 4) Both light and microbial presence are apparently required to produce any significant degradative effect under these conditions.
- 5) Since this study is inconsistent with, and even contradictory to, other studies, in both experimental conditions and results, and was done under conditions very different from expected use, it is not acceptable.

Although the report does not so state, the most likely sterilization method is autoclaving (steam heat under pressure). Besides inactivating microorganisms, this alters soil properties unpredictably, and the results from such a study are not necessarily useful predictors of environmental behavior. A curious result is that a small amount of radioactive CO_2 was apparently detected, but no other degradates -- the compound remaining after this release should also contain radiocarbon label and be distinguishable from parent. The applicant should provide a clarification of this observation.

The metabolites HOE 064619 and 085355 were formed only in light. HOE 061517 was formed in both light and dark, but represented a greater proportion of applied material in the light-exposed sample (0 - 8% vs 6 - 21%).

HOE 085355 (the first degradate in the proposed chain) is the parent **plus** an acetyl group added to the amino and **minus** the ammonium ion.

HOE 061517 (next in the chain) has a carbonyl group substituted for the amino group.

HOE 064619 (third in the chain) is HOE 061517 minus a methylene group.

Reported results can be summarized as follows:

sterile dark -- produced no detectable degradates

sterile light-exposed -- produced a small amount of CO₂

non-sterile dark -- extrapolated half life ca 300 days -- produced HOE 061517 (0 - 8%), no CO₂

non-sterile light-exposed -- extrapolated half-life 35 days -- produced HOE 061517 (6 - 21%), 064619, 085355, and CO₂

Since a new study must be performed, the applicant should note the following:

- 1) temperature should be controlled within closer tolerances, usually + 1 C on the average, although it is recognized that wider fluctuations may occur at the beginning and end of irradiation periods.
- 2) a study using sterile soil is additional information and may be useful, but is not required.

VIII. CBI Information Addendum: attached